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## VIOLARITE AND OTHER RARE NICKEL SULPHIDES\*

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### INTRODUCTION

This paper is in large measure a sequel to one by Buddington describing the nickel minerals of certain localities in southeastern Alaska.<sup>1</sup> Buddington found that in all of the nickel-bearing localities examined, the mineral associations are almost identical and that they bear a close resemblance to those at Sudbury. The inclosing rock is basic, usually a fresh, relatively coarse-grained gabbro. The ore minerals replace the rock minerals. Pyrrhotite predominates; chalcopyrite is always present and in places is relatively abundant; the chief nickel mineral is pentlandite. These three minerals are approximately of the same age. In addition, in most of the localities cited, there is a violet-colored nickel-iron sulphide which replaces pentlandite. The replacing mineral occurs as tiny veinlets following cleavages and other cracks in pentlandite and along the boundaries between pentlandite and the other ore minerals. The appearance of these veinlets is almost identical with that of supergene chalcocite replacing chalcopyrite, bornite, and other hypogene minerals. Buddington concludes that the violet-colored mineral is supergene. He notes the difficulty in isolating the mineral for analysis and refers to it in his paper as "nickel mineral X."

About the same time, Lindgren and Davy published a description of the Key West nickel mine, Nevada.<sup>2</sup> They note the same relationship; a violet-colored nickel mineral replaces pentlandite in structures which convince them that the violet mineral is supergene. They compare this mineral with a violet-colored nickel

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<sup>1</sup> Buddington, A. F., Alaskan Nickel Minerals. *Econ. Geology*, vol. 19, pp. 521-541, 1924.

<sup>2</sup> Lindgren, W. and Davy, W. M., Nickel Ores from Key West mine, Nevada. *Econ. Geology*, vol. 19, pp. 309-319, 1924.

sulphide from the Vermilion mine, Sudbury, Ontario, which for many years has been described as polydymite, and they conclude that the two minerals are identical. They question the identity of the Sudbury mineral with polydymite and conclude that it is a new mineral. They propose for it the name violarite in consideration of its violet color, and assign to it the provisional formula  $\text{NiS}_2$ . Before publishing his own paper, Buddington examined the Key West specimens collected by Lindgren and Davy and found that the violet-colored mineral from Key West was identical with nickel mineral X. He is not convinced, however, that nickel mineral X, and the Sudbury violarite are identical.

In addition to the Alaskan localities, Buddington describes nickel ores from the following localities; Dracut, Mass., Pigeon Point, Minn., Gap, Pa., and the Friday mine, Julian, Cal. In all of these except the Friday specimens, nickel mineral X replaces pentlandite in structures indicating a supergene origin.

The present authors obtained additional material from Sudbury, Ont., the Emory Creek mine, Yale, B. C., and the Floyd County nickel mine, Virginia. In addition Prof. Buddington very kindly placed at their disposal, his entire collection of nickel ores including specimens and polished sections.

A very complete suite of some 200 polished sections of ores from Sudbury, collected by Wandke and Hoffman<sup>3</sup> was also studied. This collection was presented by them to the Laboratory of Economic Geology, Harvard University.

The microscopic examinations and preparations of the samples for analysis were made by Mr. Short and the chemical analyses of violarite were made by Mr. Shannon.

#### VIOLARITE, $(\text{Ni, Fe})_3\text{S}_4$ AT SUDBURY

**OCCURRENCE.** The Vermilion mine, Sudbury, is not of great economic importance and its total production is insignificant in comparison with the great Creighton and Frood mines.<sup>4</sup> It has not been in operation for several years. It is, however, noted for its unusual mineral association and as the place of discovery of two new minerals, sperrylite,  $\text{PtAs}_2$  and violarite. Other minerals noted are chalcopyrite, bornite, chalcocite, and millerite. The pres-

<sup>3</sup> Wandke, Alfred and Hoffman, R., A study of the Sudbury ore deposits. *Econ. Geology*, vol. 19, pp. 169-204, 1924.

<sup>4</sup> Report of the Royal Ontario Nickel Commission, Toronto, 1917, p. 155.

ence of pentlandite in Vermilion ores has been reported by several authors. None of the specimens examined by us contains pentlandite, and it is probable that this mineral has been confused with millerite which it resembles. Another peculiarity of the Vermilion ores examined by us which appears significant is the total absence of pyrrhotite. Whether pyrrhotite is present at all in Vermilion ores we are not prepared to say, but the presence of violarite seems to exclude the presence of both pyrrhotite and pentlandite in these ores.

Violarite in Vermilion ores occurs as nodules and irregularly shaped areas in chalcopyrite. Where any relationship between the two minerals can be observed, chalcopyrite is later than violarite. (See Fig. 6). Surrounding the violarite areas are zones of millerite, NiS. The boundary between millerite and chalcopyrite is sharp; between millerite and violarite it is hazy and irregular. (See Figs. 5 and 7). In some areas only faint tinges of violet and the remnants of an inherited cubic cleavage reveal the "ghosts" of the replaced violarite. In other sections millerite replaces violarite in irregular veinlets traversing the violarite areas (Fig. 9). The evidence is conclusive that millerite is later than violarite, and the structures shown by the two minerals indicate that the replacing mineral is supergene.

Violarite is distinctly earlier than quartz. Figure 9 shows well formed quartz prisms of hexagonal and triangular cross-section. These quartz crystals align themselves along the cleavage cracks of violarite and several even retain the cleavage of violarite. If this violarite is supergene, then the quartz which is of later deposition must likewise be supergene. It is known that quartz is deposited by cold solutions but this type of quartz tends to form exceedingly fine interlocking grains, such as the structure at chert. Well formed hexagonal prisms formed by replacement of least suggest, if not prove, deposition by thermal solutions. As already mentioned chalcopyrite, which is the principal mineral in the Vermilion, is later than violarite. Chalcopyrite is hypogene in the ores of the principal mines at Sudbury, and there is no evidence that it is not also hypogene in the ores of the Vermilion mine.

There is one possibility which might explain the Vermilion violarite as of supergene origin, namely, that violarite replaced pentlandite and that the replacement was carried to completion, leaving no remnants of unreplaced pentlandite. Pentlandite is the chief

nickel mineral at Sudbury and it is surprising to find it absent in any nickel ores from that locality. In studying the ores from Gap, Pa., and from the Admiralty mine, Alaska, nickel mineral X replaces pentlandite and the replacement is so complete, that unreplaced areas of pentlandite are hard to find.

On the other hand violarite occurs in two other Sudbury mines, the Levack and the Worthington, and individual specimens where violarite is present, pentlandite is completely absent. And yet pentlandite is the principal nickel mineral in both mines but violarite is absent in specimens containing pentlandite. The inference is that unknown conditions of very limited extent caused the elements to precipitate locally as violarite rather than as pentlandite.

Again, supergene sulphide enrichment is rarely complete. Inspection of polished sections of sooty chalcocite ores of Ducktown, Tennessee, where enriching conditions were most intense will always reveal remnants of unreplaced pyrite, chalcopyrite and sphalerite. At Sudbury, on the other hand, oxidation and enrichment were feeble at best. The country was intensively glaciated in geologically recent times, and hard massive sulphides can be seen outcropping at the surface. Hence, if Sudbury violarite were due to supergene replacement of pentlandite, it would be expected some of the specimens would have some remnants of unreplaced pentlandite. On the contrary, as already stated, pentlandite and violarite are mutually exclusive in the Sudbury specimens examined by us.

Could the cubic cleavage, now seen in violarite, have been inherited from pentlandite, likewise an isometric mineral? This possibility is very slight. Pentlandite has a rough cubic cleavage, often not observed. Violarite has a perfect cubic cleavage, almost equal to that of galena. (Figs. 9 and 10). It is certain that the cleavage now seen in violarite is a property of that mineral.

For the above reasons the authors conclude that the Sudbury violarite is hypogene.

The presence of violarite in the Levack and Worthington ores was first noted by Wandke and Hoffman. In both mines the violarite was obtained at relatively shallow depths. The proportion of specimens containing violarite to the total number of specimens collected by them from these mines is very small and the presence of the violarite was not revealed until the ores were studied under

the microscope. The violarite-bearing ores from the Levack and Worthington contain pyrrhotite, although only sparingly; on the other hand in pentlandite-bearing ores from these mines, pyrrhotite is abundant.

PHYSICAL PROPERTIES AND COMPOSITIONS OF VIOLARITE. Violarite under the reflecting microscope is distinctly violet in ordinary (unpolarized) vertically reflected light. In some of the Sudbury specimens the mineral is isotropic in polarized light; in other specimens the areas between isometric cleavage cracks appear as small interlocking grains of weak anisotropism and diverse optical orientation. This strongly suggests that violarite deposited as an isometric mineral but some areas either inverted on cooling or underwent some small chemical alteration resulting in a mineral of lower symmetry.

The etch tests on the polished section are as follows:  $\text{HNO}_3$ —slowly effervesces and stains brown to black;  $\text{HCl}$ —no effect on surface but drop turns yellow or green;  $\text{KCN}$ ,  $\text{FeCl}_3$ ,  $\text{KOH}$ ,  $\text{HgCl}_2$ —all negative.

Violarite was discovered in the Vermilion mine early in the history of Sudbury and was analyzed by F. W. Clarke and Charles Catlett in 1889.<sup>5</sup> Their analysis after calculating the copper present as chalcopyrite is as follows:

|    |        |
|----|--------|
| S  | 41.35  |
| Ni | 43.18  |
| Co | ...    |
| Fe | 15.47  |
|    | <hr/>  |
|    | 100.00 |

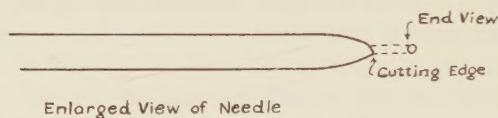
From this they derived the formula  $\text{Ni}_3\text{FeS}_5$  and considered that the mineral is identical with polydymite whose formula as given in all texts is  $\text{Ni}_4\text{S}_5$ .

Their work, however, was done before the advent of the reflecting microscope and they did not recognize the presence of millerite, hence their analysis is too high in nickel.

The present authors secured from the U. S. National Museum a specimen of Vermilion ore in which the violarite occurs as nodules up to 0.5 cm. diameter (see Figs. 5-7). Millerite surrounds the

<sup>5</sup> *Am. J. Sc.*, (3) vol. 39, p. 373, 1889.

nodules but is not included in them. Ten polished sections of this specimen were prepared. Under microscopic observation these were scratched with a No. 6 Sharps needle, and a crater-like cavity was gouged out of each violarite nodule and the powder collected. Care was taken not to overlap the violarite boundaries into the surrounding millerite and chalcopyrite nor to dig so deeply as to penetrate beneath the nodules. When all the powder that could be collected from these 10 specimens was obtained, new surfaces were ground on the sections, care being taken to grind below the craters already gouged out. The surfaces were then re-polished and scratched with the needle as before. This process was continued until the material from 40 polished sections was obtained. It was found that a sharp needle caused the fragments to fly over the surface and it was difficult to prevent the needle from slipping over the boundaries of the violarite. This difficulty was removed by grinding off the end of the needle by holding it against a rapidly revolving carborundum wheel, the axis of the needle forming an angle of about  $70^\circ$  with the surface of the wheel. In this manner a surface of elliptical cross-section was formed at the end of the needle, the former point being a frustum of a cone as shown in



sketch. The lower or protruding edge of the needle was pushed downward and into the violarite areas, the powder being shoved just ahead of the needle and reposing at the far edge of the cavity.<sup>6</sup> The best results are obtained by working the needle back and forth and if necessary rotating it slightly to jar loose the mineral particles.

The material thus obtained weighed approximately 0.25 gm. It was passed through a 100 mesh screen, and the gangue was removed by floating in methylene iodide. The part which sank was carefully washed, dried and examined under a binocular microscope. A few particles of chalcopyrite were observed, otherwise the material appeared to be pure violarite.

<sup>6</sup> The needle was held in a needle-holder with an adjustable chuck; this needle-holder can be obtained from dental supply firms for approximately eighty cents.

The analysis gave the following results and ratios:

|           |       | Ratios | Ratios after calculating<br>Cu as $\text{CuFeS}_2$ |
|-----------|-------|--------|----------------------------------------------------|
| Insoluble | 0.40  | ....   | ....                                               |
| Nickel    | 38.68 | .659   | .659                                               |
| Cobalt    | 1.05  | .018   | .018                                               |
| Copper    | 1.12  | .017   | ....                                               |
| Iron      | 17.01 | .305   | .288                                               |
| Sulphur   | 41.68 | 1.300  | 1.266                                              |
|           |       |        | $1.266 = 4 \times .317$                            |
|           | 99.94 |        |                                                    |

Calculating the copper present as chalcopyrite ( $\text{CuFeS}_2$ ) the formula obtained is  $(\text{Ni, Fe})_3\text{S}_4$ . The ratio of nickel to iron is approximately 2:1, which would yield the formula  $\text{FeS} \cdot \text{Ni}_2\text{S}_3$ . The mineral is thus a member of the linnæite ( $\text{Co}_3\text{S}_4$ ) family.

#### MILLERITE $\text{NiS}$ AT SUDBURY

The presence of millerite in Vermilion ores in close association with violarite was first noted by the authors. Previous observers mistook this mineral for pentlandite. Millerite differs from pentlandite in that it is strongly anisotropic whereas pentlandite is isotropic. Consequently it is not surprising that before the use of the polarizing reflecting microscope became general, the presence of millerite was unsuspected.

Millerite is somewhat harder than violarite and stands up in relief above it. The properties of pentlandite and millerite are compared in tabular form as follows:

| PENTLANDITE, $(\text{Ni, Fe})\text{S}$                 | MILLERITE, $\text{NiS}$                                              |
|--------------------------------------------------------|----------------------------------------------------------------------|
| Color, pale brass yellow; almost identical with pyrite | Pale brass yellow; almost identical with pyrite.                     |
| Isotropic.                                             | Strongly anisotropic.                                                |
| Rough cubic cleavage.                                  | No cleavage.                                                         |
| No prismatic structure.                                | Some specimens have prismatic structure; others lack it.             |
| Easily scratched by needle.                            | Scratched with difficulty.                                           |
| <i>Etch tests</i>                                      | <i>Etch tests</i>                                                    |
| $\text{HNO}_3$ .....slowly stains iridescent.          | $\text{HNO}_3$ .....slowly stains iridescent.                        |
| $\text{HCl}$ .....negative.                            | $\text{HCl}$ .....negative.                                          |
| $\text{KCN}$ ....."                                    | $\text{KCN}$ ....."                                                  |
| $\text{FeCl}_3$ ....."                                 | $\text{FeCl}_3$ ....."                                               |
| $\text{KOH}$ ....."                                    | $\text{KOH}$ ....."                                                  |
| $\text{HgCl}_2$ ....."                                 | $\text{HgCl}_2$ .....Stains brown in places.<br>Some areas negative. |

The presence of millerite at Sudbury was noted by Barlow many years ago.<sup>7</sup> The occurrence observed was in the Copper Cliff mine 150 feet below the surface. It was regarded as supergene and a replacement of pentlandite.

#### VIOLARITE AT JULIAN, CALIFORNIA

The nickel ores of the Friday mine, Julian, California, have been studied by F. C. Calkins,<sup>8</sup> Tolman and Rogers,<sup>9</sup> Hudson,<sup>10</sup> and Buddington.<sup>11</sup> The writers had the use of Calkins's original collection, now in the U. S. National Museum.

The deposit lies near the crest of the range between San Diego and the Imperial Valley. The range proper is a northward continuation of the mountain system which forms the backbone of Lower California. This range, which is predominantly granitic in character, is invaded by a stock of gabbro which has an area at the surface of at least one square mile. The ores occur as irregular replacements in this gabbro. Pyrrhotite predominates; chalcopyrite is abundant in places. Tolman and Rogers, also Hudson, report the presence of pentlandite. Calkins, Buddington and the present authors failed to observe that mineral. The nickel mineral is intergrown with pyrrhotite and chalcopyrite in patterns indicating that it is contemporaneous with those minerals. At least there are no textures suggesting replacement as far as the three minerals mentioned are concerned. Later than these three minerals and traversing them in veinlets is a hard pale brass colored mineral. Calkins calls this mineral pyrite but Buddington suggests that it may be marcasite. Inspection in reflected polarized light shows that the mineral is isotropic, hence it is probably pyrite. Still later than pyrite are siderite veinlets (called calcite by previous writers) which traverse the entire section including the pyrite veinlets.

The nickel mineral was called polydymite by Calkins; it has the following properties:—

<sup>7</sup> Barlow, A. E., The Sudbury Mining District. *Geological Survey of Canada, Annual Report*, vol. 14, Part H, p. 98, 1904.

<sup>8</sup> Calkins, F. C., An occurrence of nickel ore in San Diego County, Calif. *U. S. Geol. Survey, Bull.* 640, pp. 77–82, 1916.

<sup>9</sup> Tolman, C. F. and Rogers, A. F., A study of the magmatic sulfid ores. *Leland Stanford Jr. Univ., Pub.*, 1916, pp. 40–41.

<sup>10</sup> Hudson, F. S., Geology of the Cuyamaca region of California. *Pub. Univ. of Calif.*, vol. 13, 1922.

<sup>11</sup> Buddington, A. F., *Op. cit.*, p. 537.

Hardness, about the same as pyrrhotite.

Color, galena white.

Isotropic.

Perfect cubic cleavage, almost equal to that of galena.

Fairly strong magnetism.

*Etch tests.*—

$\text{HNO}_3$  effervesces; mineral turns dark.

$\text{HCl}$  no effect on surface but drop colors yellow or green.

$\text{KCN}$  negative.

$\text{FeCl}_3$  negative.

$\text{KOH}$  negative.

$\text{HgCl}_2$  negative.

These properties correspond exactly or very nearly so to those of polydymite from the type locality,—Grunau, Westphalia. The size of the areas of the nickel mineral as shown in polished sections of Friday ores gave a promise of obtaining material sufficiently pure for analysis. Material from 40 polished surfaces was obtained by scratching the surfaces with the needle in the manner already described for Sudbury violarite.

The total amount of material obtained was about 0.12 gm. It was pure except for siderite which crossed the mineral, in minute branching veinlets (see Fig. 4), and a few grains of chalcopyrite. The removal of this siderite was a problem of some difficulty. It is too near the nickel mineral in specific gravity to allow separation by means of heavy liquid. The electromagnet could not be used for this purpose as both siderite and the nickel mineral are magnetic. The method adopted was to dissolve out the siderite by gentle warming in 1:1  $\text{HCl}$ . This method involves some risk as some sulphides are measurably soluble in  $\text{HCl}$ . Inspection of the material after this treatment showed that the sulphide had not been acted on by the acid. The remaining material was placed in a separatory funnel containing heavy solution and the quartz and other insoluble gangue minerals were floated off.

Analysis of the sulphide residue gave the following results, the copper being again calculated as chalcopyrite:

|           |       | Ratios | Ratios after calculation<br>of Cu as $\text{CuFeS}_2$ |
|-----------|-------|--------|-------------------------------------------------------|
| Insoluble | 1.31  | ....   | ....                                                  |
| Nickel    | 33.94 | .578   | .578                                                  |
| Cobalt    | 2.50  | .042   | .042                                                  |
| Copper    | 1.05  | .017   | ....                                                  |
| Iron      | 19.33 | .346   | .329                                                  |
| Sulphur   | 42.17 | 1.315  | 1.281                                                 |

$.949 = 3 \times .316$   
 $1.281 = 4 \times .320$

The formula obtained is  $(\text{Ni, Fe})_3\text{S}_4$ .

The results are almost identical with those yielded by the Vermilion material. This mineral is undoubtedly violarite, in spite of its lack of a violet color. The Friday violarite contains more cobalt than the Vermilion ore and this may account for its white color.

#### POLYDYMITE, $\text{Ni}_3\text{S}_4$

Polydymite has been reported by many authors from many localities but in every instance when their description is checked or their material examined in the reflecting microscope, the supposed polydymite has proved to be another mineral, usually violarite. As far as known, genuine polydymite has never been noted in a North American locality and the only place where it is definitely known to occur is the type locality, Grunau, Westphalia.

A specimen from that locality examined microscopically in polished section gave the following properties:

Color—white with a tinge of yellow.

Hardness—readily scratched by needle.

Isotropic.

Rough cubic cleavage.

##### *Etch tests.*

$\text{HNO}_3$  effervesces slowly; mineral darkens.

$\text{HCl}$  no effect on mineral; drop turns yellow.

$\text{KCN}$  negative.

$\text{FeCl}_3$  negative.

$\text{KOH}$  negative.

$\text{HgCl}_2$  negative.

The analysis after deducting for impurities is S 41.09, Ni 54.30, Co 0.63, Fe 3.98 = 100 (Dana: *System of Mineralogy*).

The formula usually given for the mineral is  $\text{Ni}_4\text{S}_5$ . Wherry and Foshag in reviewing the analysis show that the formula is more probably  $\text{Ni}_3\text{S}_4$ .<sup>12</sup> In view of the very close similarity in physical properties and etch tests of polydymite to violarite, that conclusion is undoubtedly correct.

Polydymite is thus the iron-and-cobalt-free end member of the isomorphous series  $(\text{Ni, Co, Fe})_3\text{S}_4$ . Linnaeite ( $\text{Co}_3\text{S}_4$ ) is the

<sup>12</sup> Wherry, E. T. and Foshag, W. F., The Sulfide Minerals. *Jour. Wash. Acad. of Sciences*, vol. 10, p. 495, 1920.

nickel-and-iron-free and member. The corresponding iron-bearing end member ( $\text{Fe}_3\text{S}_4$ ) has not been reported.

SIEGENITE  $(\text{Ni},\text{Co})_3\text{S}_4$  IN MADISON CO., MO.

The presence of siegenite in southeastern Missouri was known prior to 1857 when an analysis of a sample from Mine la Motte, Madison County, was made by Genth. (See Dana: *System of Mineralogy*). This mineral is usually reported as linnaeite, but in Madison County the percentage of nickel usually exceeds that of cobalt, hence siegenite is a more correct designation.

Siegenite occurs closely associated with chalcopyrite and galena in the disseminated lead ores of the region. It was formerly obtained as a by-product from the concentration of lead ores, but deeper exploration revealed the presence of comparatively rich cobalt-nickel-copper sulphides with lesser amounts of lead. These ores are found at the base of the Bonneterre dolomite (Cambrian) and extend into the underlying Lamotte sandstone (Cambrian). The most extensive deposits are those of the Missouri Cobalt Co, formerly the North American Lead Co., Fredericktown, Mo., and were worked prior to 1920 when the property was closed down.<sup>13</sup>

A specimen of ore from this property was donated to the authors by Mr. C. E. Siebenthal. Examined in polished section, it was found to consist of about equal proportions of sulphides and gangue minerals, the latter being chiefly quartz with a smaller proportion of shale. The sulphides were estimated to consist of approximately 45% chalcopyrite, 45% siegenite and 10% galena. A notable feature is the total absence of pyrite and pyrrhotite from the specimen. The minerals were very fine grained and so intimately admixed that there was no possibility of isolating the siegenite for analysis. However, the accompanying sulphides, chalcopyrite and galena, are easily deducted in a calculation based on an analysis of the whole sample. The sample was crushed to 80 mesh and was passed twice through a separatory funnel containing methylene iodide in order to eliminate as much of the gangue as possible. The resultant product was analyzed by Mr. J. G. Fairchild of the U. S. Geological Survey with the following results:

<sup>13</sup> Buehler, H. A., Biennial report of the State Geologist, *Missouri Bureau of Geology and Mines*, pp. 55-56, 1919,

|           |        | Ratios | After<br>deduction<br>of PbS | After<br>deduction<br>of CuFeS <sub>2</sub> |
|-----------|--------|--------|------------------------------|---------------------------------------------|
| Insoluble | 11.88  | ....   | ....                         | ....                                        |
| Lead      | 9.40   | .045   | ....                         | ....                                        |
| Copper    | 13.10  | .206   | .206                         | ....                                        |
| Iron      | 15.17  | .271   | .271                         | .065                                        |
| Cobalt    | 8.72   | .148   | .148                         | .148                                        |
| Nickel    | 11.27  | .192   | .192                         | .192                                        |
| Sulphur   | 30.57  | .953   | .908                         | .496                                        |
|           |        |        |                              | .496 = 4 × .124                             |
|           | 100.11 |        |                              |                                             |

The formula may be expressed  $(\text{Ni}, \text{Co}, \text{Fe})_3\text{S}_4$ . This analysis is compared with an earlier analysis as follows:

Siegenite, calculated from above analysis:

| Ni    | Co    | Fe   | S     | Pb   | Insol. |          |
|-------|-------|------|-------|------|--------|----------|
| 28.52 | 22.02 | 9.21 | 40.25 | .... | ....   | = 100.00 |

Siegenite, analyzed by F. A. Genth, 1857:

| Ni    | Co    | Fe   | S     | Pb   | Insol. |         |
|-------|-------|------|-------|------|--------|---------|
| 30.53 | 21.34 | 3.37 | 41.54 | 0.39 | 1.07   | = 98.34 |

Microscopic examination of a polished section of siegenite from the same specimen gave the following results:

Color—cream with a tinge of yellow; indistinguishable from that of linnaeite.

Hardness—harder than chalcopyrite but scratched readily by needle.

Isotropic.

No cleavage pits observed.

*Etch tests.*—

$\text{HNO}_3$  slowly effervesces and stains brown; brings out scratches.

HCl negative.

KCN negative.

$\text{FeCl}_3$  negative.

KOH negative.

$\text{HgCl}_2$  seems to stain in places; doubtful.

The above properties are very similar to those of both polydymite and linnaeite. They differ from those of violarite from Julian, Cal., which likewise contains cobalt, in the absence of a perfect cubic cleavage and in the yellower color of siegenite.

#### BRAVOITE $(\text{Ni}, \text{Fe})\text{S}_2$

Bravoite was first discovered in the vanadium mines at Minera, Peru, and was analyzed and described by Hillebrand.<sup>14</sup> The

<sup>14</sup> Hillebrand, W. F., *Amer. Journal of Science*, Ser. 4, vol. 24, p. 151, 1907.

analysis after the deduction of impurities was as follows:

Ni 18.23, Fe 29.46, S 52.31.

From this Hillebrand derived the formula  $(\text{Fe}, \text{Ni})\text{S}_2$  and considered that the mineral was nickeliferous pyrite.

Buddington obtained material collected by D. F. Hewett from the type locality, polished the ore and examined it microscopically. He makes the following observations<sup>15</sup>:

"The mineral occurs as grains in 'quisquite.' With reflected light it has a pallid gray color with a violet hue and shows three well-defined intersecting cleavages. Its hardness is a little less than 5. Etch tests gave the following results:  $\text{HNO}_3$ —effervesces and turns blue gray;  $\text{HCl}$ ,  $\text{HgCl}_2$ ,  $\text{KCN}$ ,  $\text{KOH}$  and  $\text{FeCl}_3$ —negative. One grain reacted slightly with  $\text{KOH}$  and rubbed faint brown."

More recently there has been available to American mineralogists, bravoite from Mechernich, Germany, which has been described by Kalb and Meyer.<sup>16</sup> The mineral occurs as individual pyritohedrons, crystal rusts, and massive. It occupies open spaces between conglomerate beds and small fissures and cavities in in the conglomerate adjacent to the main lead-zinc ore body at Mechernich. The crystals have a remarkable zonal structure which is especially apparent on polished surfaces. Zones of a violet-colored mineral alternate with zones of a brass yellow mineral, the boundaries of the zones paralleling the pyritohedral planes. (See Fig. 8). The violet colored zones do not all have the same tinge of violet; a zone of light-violet mineral may lie adjacent to a zone of deep-violet mineral, or a zone of deep-violet mineral may be separated from a zone of light violet mineral by one of the brass-yellow mineral. Material from one of the violet-colored zones and from one of the brass-yellow zones were analyzed separately by the authors cited, with the following results:

|                     | Ni    | Co   | Fe    | Cu   | S     | Insol. |
|---------------------|-------|------|-------|------|-------|--------|
| Violet-colored zone | 24.73 | 3.28 | 17.08 | 0.47 | 51.15 | 0.40   |
| Yellow-colored zone | 4.40  | tr.  | 38.02 | 2.80 | 50.77 | 2.50   |

The formula for both zones can be expressed as  $(\text{Ni}, \text{Fe})\text{S}_2$ . The above authors state that the violet-colored zone can be termed "bravoite" and the yellow zone "nickeliferous pyrite." The different shades of violet, are probably due to different proportions of

<sup>15</sup> *Op. cit.*, p. 526.

<sup>16</sup> Kalb, G. and Meyer, Emil, Die Nickel-und Kobaltführung der Knottenerz-lagerstätte von Mechernich. *Centralbl. f. Mineral., Abt. A.*, p. 26, 1926.

nickel and iron.<sup>17</sup> The present authors obtained a specimen of Mechernich bravoite through the kindness of Dr. Buddington. Examined microscopically in reflected light it gave the following properties:

Color—violet gray.

Hardness—cannot be scratched by needle (greater than 5.5).

Isotropic.

No indication of cleavage.

*Etch tests.*—

HNO<sub>3</sub>. Fumes tarnish; mineral stains iridescent and brings out zonal structure.

HCl, KCN, FeCl<sub>3</sub>, KOH, HgCl<sub>2</sub>—negative.

These properties are very different from those of the mineral from Minaragra as reported by Buddington. The Mechernich mineral occurs in well-formed crystals up to one centimeter in diameter and unmixed with other minerals. The Minaragra mineral was not examined under the reflecting microscope by Hillebrand before analysis and the present writers are inclined to question this analysis. On the other hand the properties of the Minaragra mineral as reported by Buddington check exactly with those of violarite. The cubic cleavage and hardness are especially significant. The present authors were unable to secure a satisfactory specimen of the Minaragra nickel mineral.

#### NICKEL MINERAL X.

The designation nickel mineral X was given by Buddington to a violet-colored nickel-iron sulphide which replaces pentlandite in veinlets following cleavage cracks, grain boundaries and other open spaces. No grains with crystal faces were observed. The properties as determined by Buddington and checked by the authors are as follows:

Color—violet grey.

Hardness—medium.

Cleavage—cubic.

*Etch tests.*—

HNO<sub>3</sub>—effervesces slowly; mineral darkens.

HCl—no effect on mineral; drop turns yellow.

KCN, FeCl<sub>3</sub>, KOH, HgCl<sub>2</sub>—negative.

<sup>17</sup> The violet tinge of bravoite was not specifically mentioned by Kalb and Meyer. They describe its color as steel-gray. It is not apparent from their description whether or not they examined the mineral in polished section, but the illustration accompanying the article seems to indicate it.

Buddington's work was done before the use of polarized reflected light became general. Observations with polarized light on polished sections from his collection were made by the authors. In specimens from some localities nickel mineral *X* is isotropic; from other localities it is weakly anisotropic.

| ISOTROPIC               | ANISOTROPIC           |
|-------------------------|-----------------------|
| Gap, Pa.                | Dracut, Mass.         |
| Tasmania claim, Alaska. | Pigeon Point, Minn.   |
| Admiralty, Alaska.      | Bohemia mine, Alaska. |
| Emory Creek, B. C.      | Floyd Co., Va.        |

The violet color is best seen where nickel mineral *X* is in contact with pentlandite. Where the replacement is nearly or entirely complete as in the Tasmania, Admiralty and Gap specimens, nickel mineral *X* is in contact with pyrrhotite, and here its violet color is somewhat obscured by that of pyrrhotite. The color of nickel mineral *X* seems to be ashy-gray in these specimens. Where the replacement is nearly complete, as in the localities mentioned, the mineral is very crumbly and tends to break down chemically when exposed to the atmosphere. This is in contrast to Sudbury violarite which is stable for long periods and led Buddington to believe that the two minerals are not identical. However, in specimens where the replacement is not far advanced, such as the Dracut, Emory Creek, Pigeon Point and Floyd County specimens, nickel mineral *X* shows no signs of being crumbly or breaking down chemically.

The ore deposits where nickel mineral *X* occurs have nearly all been well described by Buddington and by Lindgren and Davy. These descriptions will not be repeated here. Two additional localities, Emory Creek, B. C., and Floyd County, Va., have also been described by others and are summarized here for convenience.

EMORY CREEK, B. C. The nickel prospect on Emory Creek, British Columbia, is well described by Cairnes.<sup>18</sup> The prevailing rocks are batholithic and have the average composition of a quartz diorite. Invading these rocks is a dike of fresh hornblendite of unknown dimensions. The country is precipitous and exploration is difficult. The ore body is a mass of nearly solid sulphide 75 feet across and outcropping as a cliff 30 feet high. Exploration had not

<sup>18</sup> Cairnes, C. E., Nickeliferous Mineral Deposit, Emory Creek, Yale Mining Division, B. C. *Geological Survey of Canada, Summary Report, 1924, Part A*, pp. 100-105.

revealed the size of the ore body at the time of Cairnes's visit. Included in the sulphide mass and in its vicinity is considerable hypersthene which appears to be of primary origin. Feldspar is absent or only sparingly present. The predominant sulphide is pyrrhotite; chalcopyrite and pyrrhotite are subordinate. Cutting pentlandite are veinlets of a mineral with nearly the color of pyrrhotite. These veinlets are confined to the pentlandite and follow cracks in it. Cairnes suspected that this mineral is identical with nickel mineral X but did not have specimens from other localities with which to make comparisons. A specimen from Emory Creek was kindly sent by Dr. Cairnes to the authors which enabled them to identify the unknown mineral in this specimen as nickel mineral X. Cairnes states that much oxidation is in evidence where the specimen was obtained. It will be interesting to find out whether or not the mineral persists in depth.

FLOYD COUNTY, VIRGINIA. Near the north border of Floyd County Virginia, is a small nickel prospect not of commercial importance. It is located near the junction of Flat Run and Lick Fork, two head water streams of the South Fork of Roanoke River. The deposit has been described by Watson<sup>19</sup> and by Ross.<sup>20</sup> Specimens of sulphide ore collected by Dr. Ross were made available to the authors for study.

According to Ross, the prevailing rocks of the region are schists and gneisses of pre-Cambrian age. Cutting these older rocks is a compound dike consisting of three distinct kinds of rocks, a dark gray fresh rock composed almost exclusively of andesine, a diabase, and a rock which varies in composition between gabbro and pyroxenite. The pyrrhotite vein is a mineralized zone in this compound dike. There are sharp boundaries between diabase, gabbro-pyroxenite and andesinite, but no sharp wall between andesinite and the inclosing wall rock was observed.

The principal sulphide mineral is pyrrhotite. Chalcopyrite and pentlandite are subordinate and sphalerite is present in places as minute inclusions in pyrrhotite. The above ore minerals are complexly intergrown and seem to be contemporaneous. Pyroxene is the principal gangue mineral in the ore specimens. The sulphides

<sup>19</sup> Watson, Thos. L., The occurrence of nickel in Virginia. *Trans. Amer. Inst. Min. Engrs.*, pp. 829-843, 1907,

<sup>20</sup> Ross, Clarence S., Copper mines of the Southern Appalachians. *U. S. Geol. Survey, Unpublished Manuscript.*

are later than pyroxene and traverse it as small branching veinlets which in part follow cleavage planes in the pyroxene. Nickel mineral *X* cuts pentlandite in tiny veinlets following open spaces. In properties it is identical with the mineral in the localities already cited.

CONCLUSION. Nickel mineral *X* and violarite are identical in color, hardness, cleavage, polarization and etch tests. Both minerals consist primarily of nickel iron and sulphur. We are therefore convinced that the two minerals are identical.

A major problem left unsolved by us is the relationship between violarite and pentlandite at Sudbury. It is known that these two minerals occur in the same mine but they have not been observed in the same hand specimen. It is hoped that this paper will induce others to undertake the solution of this problem.

#### SUMMARY

Violarite from Sudbury and the unknown nickel mineral from the Friday mine, Julian, California, were both analyzed and found to be identical. The chemical formula determined is  $(\text{Ni, Fe})_3\text{S}_4$ ; the mineral belongs in the isometric system and is closely similar in physical and chemical properties to linnaeite,  $\text{Co}_3\text{S}_4$  and polydymite,  $\text{Ni}_3\text{S}_4$ . The authors believe that violarite from these two localities is hypogene. Nickel mineral *X* and violarite have the same physical properties and contain the same elements, hence are believed to be identical.

FIG. 1. Violarite (supergene) replacing pentlandite in veinlets which follow cleavage cracks and other open spaces. Violarite veinlets do not extend into surrounding pyrrhotite. Dracut, Mass., nickel mine.  $\times 83$ .

FIG. 2. Violarite (supergene) replacing pentlandite. A more advanced stage of replacement than shown by Fig. 1. Pigeon Point, Minn.  $\times 200$ .

FIG. 3. Violarite (supergene) replacing pentlandite. A still more advanced stage of replacement. Only a few small remnants of pentlandite have survived attack. Gap, Pa.,  $\times 300$ .

FIG. 4. Violarite (hypogene) surrounded by chalcopyrite and pyrrhotite. The violarite boundaries are straight. Violarite here shows tendency to form crystal planes. Veinlets of siderite follow cleavage cracks and fill triangular cleavage pits in violarite. Perfect cubic cleavage of violarite clearly shown in lower part of picture. Friday mine, Julian, Cal.  $\times 38$ .

- VI violarite,  $(\text{Ni, Fe})_3\text{S}_4$
- Pn pentlandite,  $(\text{Ni, Fe})\text{S}$
- Po pyrrhotite,  $\text{FeS} + \text{S}$
- S siderite,  $\text{FeCO}_3$
- Cp chalcopyrite



FIG. 1.

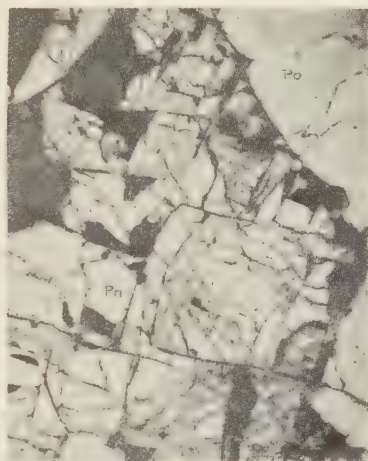


FIG. 2.

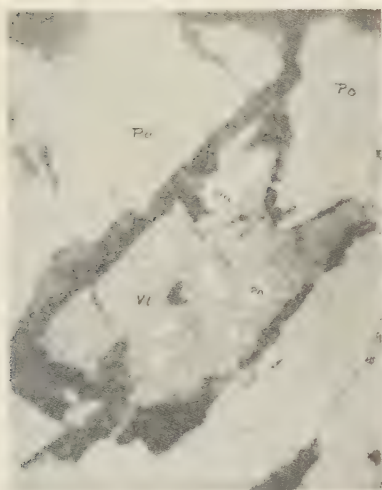


FIG. 3.

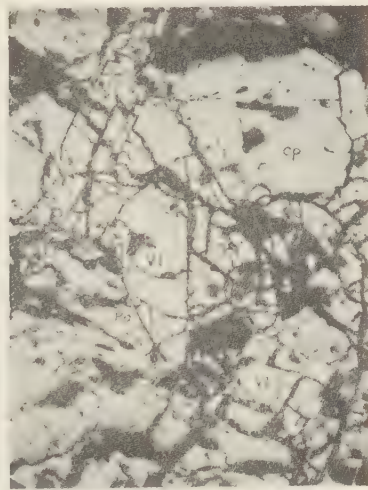


FIG. 4.

FIG. 5. Millerite (probably supergene) halos surrounding violarite (hypogene). Boundaries between millerite and chalcopyrite are sharp. Where millerite is absent, boundaries between violarite and chalcopyrite are sharp. Boundaries between millerite and violarite are fuzzy. Violarite "nodules" are composed of aggregates of small grains of diverse orientation. This is better shown in Fig. 7. Vermilion mine, Sudbury, Ont.  $\times 38$ .

FIG. 6. Chalcopyrite veinlets crossing violarite. Chalcopyrite is apparently later than violarite. There is a possibility however that violarite completely replaces some pre-existing mineral which was earlier than chalcopyrite; if this were true, violarite could be later than chalcopyrite. Violarite areas are rimmed by millerite. Vermilion mine, Sudbury, Ont.  $\times 38$ .

FIG. 7. Millerite replacing violarite. A more advanced stage than that shown in Fig. 5. Vermilion mine, Sudbury, Ont.  $\times 60$ .

FIG. 8. Concentric shells of bravoite and nickeliferous pyrite. In the bravoite areas different shades of violet paralleling the pyrite bands are clearly seen. The pyrite areas parallel pyritohedral crystal faces. Mechernich, Germany.  $\times 246$ .

MI millerite  $\text{NiS}$   
VI violarite  $(\text{Ni, Fe})_3\text{S}_4$   
Cp chalcopyrite,  $\text{CuFeS}_2$   
Br bravoite  $(\text{Ni, Fe})\text{S}_2$   
Py pyrite (nickeliferous),  $(\text{Fe, Ni})\text{S}_2$



FIG. 5.



FIG. 6.



FIG. 7

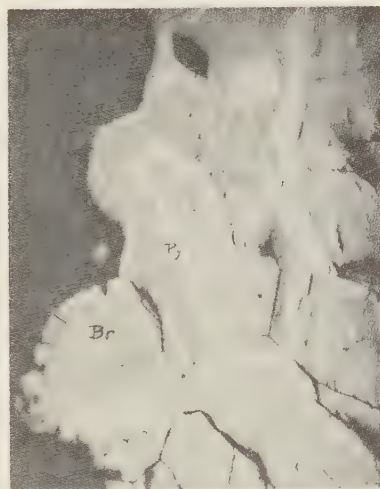


FIG. 8.



FIG. 9.



FIG. 10.

FIG. 9. Violarite showing perfect cubic cleavage. Quartz crystals are replacing violarite, the quartz boundaries in part aligned along cleavage faces of violarite. Some of the cleavage cracks of violarite extend into the quartz areas, showing that quartz has inherited cleavage of violarite. Millerite is replacing violarite, the replacement following irregular cracks. Levack mine, Sudbury, Ont.  $\times 60$ .

FIG. 10. Violarite showing perfect cleavage being replaced by millerite. Levack mine, Sudbury, Ont.  $\times 20$ .

VI violarite  
Ml millerite  
Q quartz

# NOTES ON AN X-RAY DIFFRACTION STUDY OF THE SERIES CALCITE-RHODOCHROSITE

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## ABSTRACT

Five analyzed specimens of manganocalcite were studied to determine the relation between the varying per cent of manganese carbonate and the optical, physical, and structural properties of the mineral. These properties were compared with those of the two end members of the group; calcite and rhodochrosite. It was found that as the mineral grades from calcite to rhodochrosite a gradual increase in the indices of refraction and the specific gravity occurs. Charts are shown giving the variation of the indices of refraction, specific gravities, and *x*-ray diffraction patterns in relation to the per cent of manganese carbonate. The structural relationship, as shown by *x*-ray diffraction patterns, is such that the variation in the isomorphous constituents can be detected by the diffraction lines representing the interplanar atomic spacing. These patterns show a gradual decrease in the length of the edge of the unit rhombohedron as the mineral grades from calcite to rhodochrosite.

Manganocalcite was first described by Poggendorff<sup>1</sup> as a definite mineral species. It was later found to contain a varying per cent of manganese carbonate which ranged from very small amounts in manganiferous calcite to almost pure manganese carbonate in rhodochrosite. Dana<sup>2</sup> uses the term, "calciferous manganocalcite," but does not give the material the rank of a definite mineral species.

The relation between the structural and the physical properties, and the variation in the per cent of manganese carbonate in the group calcite-rhodochrosite has always been a matter of much interest. The physical properties of the mineral have been described<sup>3</sup> in detail, and it has been shown that in general a uniform rate of variation exists, between the two extremes of the series. The variation in the internal structure, as portrayed by the *x*-ray diffraction patterns taken in this work, also shows a uniform rate of change. New optical determinations, however, were necessary, because those at present in the literature are limited to a single value for the index of refraction determined by Sundius<sup>4</sup> on manganocalcite containing 20 molecular per cent manganese carbonate.

In the present work specimens of analyzed manganocalcite have been studied in an attempt to correlate physical, optical, and

<sup>1</sup> Poggendorff, J. C., *Annalen der Physik und Chemie*, vol. 69, p. 429, 1846.

<sup>2</sup> Dana, E. S., *System of Mineralogy*, 6th Edition, p. 278, 1892,

<sup>3</sup> *Op. cit.*

<sup>4</sup> Sundius, N., *Tsch. Min., Pet. Mit.*, vol. 38, p. 175, 1925.

chemical relationships with *x*-ray diffraction patterns. The indices of refraction were determined by the immersion method, the specific gravities determined by the use of a pycnometer, and the *x*-ray diffraction patterns obtained by the powder method of Hull<sup>5</sup> and Debeye-Scherrer.<sup>6</sup>

The writer is indebted to Dr. Paul F. Kerr, of the Department of Geology and Mineralogy, Columbia University, for suggesting and outlining the problem, and for his advice as the work progressed. The investigation has been greatly aided through the cooperation of Dr. C. S. Ross, of the U. S. Geological Survey, and Mr. L. H. Bauer, of the New Jersey Zinc Co. Through their kindness specimens of manganocalcite have been secured together with accompanying analyses giving the manganese carbonate content. Thanks are also due to Mr. Earl V. Shannon, Mr. J. G. Fairchild, and Mr. J. J. Fahey for analyses of specimens.

The specimen of manganocalcite first described by Poggendorff<sup>7</sup> in 1846 was thought to be isomorphous with aragonite. Later work by Krenner<sup>8</sup> in 1884 proved it to be rhombohedral. This work placed it among the group of isomorphous rhombohedral carbonates which includes calcite, rhodochrosite, siderite, smithsonite, and magnesite. The earliest analysis of manganocalcite in the literature was made by Poggendorff in which he obtained 67.48 per cent manganese carbonate. A later analysis of manganocalcite from Franklin, New Jersey, by Roepper<sup>9</sup> in 1870 gave 43.54 per cent manganese carbonate, while Weibull<sup>10</sup> in 1885 obtained 11.30 per cent and 40.31 per cent manganese carbonate in material from Wester Silfberg. Thus it appears that early analyses of the mineral show considerable variation in the content of manganese carbonate.

Five samples of the mineral from four different localities, each with a different per cent of manganese carbonate, have been examined in this work. These, with the two end members of the group, calcite and rhodochrosite, are listed in Table I, together with the locality and analysis of each. The range from zero per cent manganese carbonate to 42.17 per cent is fairly well covered by the analyses. No material was secured, however, with a man-

<sup>5</sup> Hull, A. W., *Physical Review*, vol. 10, pp. 661-669, 1917.

<sup>6</sup> Debeye, P., and Scherrer, P., *Phys. Zeitsch.*, vol. 17, p. 277, 1916.

<sup>7</sup> *Op. Cit.*

<sup>8</sup> Krenner, J. A., *Zeit. f. Kryst.*, Vol. 8, p. 242, 1884.

<sup>9</sup> Roepper, W. T., *Amer. Jour. Science*, vol. 50, p. 37, 1870.

<sup>10</sup> Weibull, Mats., *Min. und Pet. Mitt.*, vol. 7, p. 111, 1885-1886.

ganese carbonate content between the 42.17 per cent of the Sparta, N. C., specimen and the 95.72 per cent of the Lake County, Colo., rhodochrosite. The samples were not entirely free from magnesium carbonate and iron carbonate, which in some places may account for slightly discordant results.

TABLE I

| %<br>MnCO <sub>3</sub> | %<br>CaCO <sub>3</sub> | %<br>MgCO <sub>3</sub> | %<br>FeCO <sub>3</sub> | %<br>ZnCO <sub>3</sub> | %<br>SrCO <sub>3</sub> | %<br>Insol. | Analyzed by                |
|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|-------------|----------------------------|
| —                      | 100.00                 | —                      | —                      | —                      | —                      | —           | —                          |
| 1.09                   | 95.32                  | 1.34                   | 0.09                   | —                      | —                      | 2.48        | J. J. Fahey.               |
| 7.00                   | 86.90                  | 2.57                   | 3.50                   | —                      | 0.24                   | —           | J. G. Fairchild.           |
| 15.40                  | —                      | —                      | —                      | —                      | —                      | —           | N. J. Zinc Co.             |
| 32.34                  | 65.98                  | Trace                  | Trace                  | 0.69                   | —                      | —           | N. J. Zinc Co.             |
| 42.17                  | 56.31                  | 1.71                   | 0.08                   | —                      | —                      | 0.25        | E. V. Shannon.             |
| 95.72                  | 0.50                   | 0.68                   | 1.87                   | —                      | —                      | —           | E. T. Wherry <sup>11</sup> |

As the mineral grades from calcite to rhodochrosite, increasing in the per cent of manganese carbonate, the indices of refraction, as generally supposed, grow correspondingly larger. A chart, (Fig. I), gives the variation in indices of refraction and specific gravities found in the five samples, compared with those determined for calcite and rhodochrosite. The data for calcite has been taken from Hastings,<sup>12</sup> and the indices of refraction for rhodochrosite were determined by Larsen<sup>13</sup> for the Lake County variety. With a small per cent of manganese carbonate, as in the sample from Kings Mt., N. C., which contained 1.09 per cent, the increase in  $\epsilon$  and  $\omega$  from that of calcite was very small;  $\epsilon = 1.490 \pm .003$ ;  $\omega = 1.662 \pm .003$ . This is but slightly higher than calcite;  $\epsilon = 1.486$ ;  $\omega = 1.658$ ; the increase in both  $\epsilon$  and  $\omega$  being .004. In the sample from Ore Knob, N. C., which contained 7.00 per cent manganese carbonate, a slightly greater increase was noticed, particularly in  $\epsilon$ . This greater increase is probably due to the presence of other isomorphous constituents which would have a tendency to increase the indices of refraction. This sample contained 3.50 per cent iron carbonate and 2.57 per cent magnesium carbonate. The two samples from Franklin, N. J., and the one from Sparta, N. C., each with a greater per cent of manganese carbonate, showed

<sup>11</sup> Wherry, E. T., *Wash. Acad. Science*, vol. 7, p. 365, 1917.

<sup>12</sup> Hastings, C. S., *Amer. Jour. Science*, 3rd Ser., vol. 35, p. 73, 1888.

<sup>13</sup> Larsen, E. S., *Wash. Acad. Science*, vol. 7, p. 365, 1917.

a gradual increase in the indices of refraction corresponding closely to the theoretical values which might be expected between calcite and rhodochrosite.

The specific gravity variations were observed to correspond; namely, as the calcium carbonate is replaced by manganese carbonate a gradual increase in the specific gravity takes place. The sample from Ore Knob, N. C., showed a greater increase in specific gravity than the 7.00 per cent manganese carbonate would warrant. The presence of iron and magnesium carbonates would easily account for this higher value. The values obtained for the remaining samples correspond closely to the theoretical values as shown on the chart in figure I. The figures obtained for the indices of refraction and the specific gravities are shown in Table 2.

TABLE II

|                                    | % $\text{MnCO}_3$ | Indices of Refraction |          | Specific Gravities |
|------------------------------------|-------------------|-----------------------|----------|--------------------|
|                                    |                   | $\epsilon$            | $\omega$ |                    |
| Calcite, C. P.                     | 00.00             | 1.486                 | 1.658    | 2.715              |
| Manganocalcite<br>Kings Mt., N. C. | 1.09              | 1.490                 | 1.662    | 2.724              |
| Manganocalcite<br>Ore Knob, N. C.  | 7.00              | 1.501                 | 1.672    | 2.824              |
| Manganocalcite<br>Franklin, N. J.  | 15.40             | 1.503                 | 1.680    | 2.856              |
| Manganocalcite<br>Franklin, N. J.  | 32.34             | 1.519                 | 1.713    | 3.021              |
| Manganocalcite<br>Sparta, N. C.    | 42.17             | 1.534                 | 1.721    | 3.143              |
| Rhodochrosite<br>Lake Co., Colo.   | 95.72             | 1.595                 | 1.817    | 3.710              |

Isomorphous variation in the structure is illustrated by the x-ray diffraction patterns reproduced in Figure 2. All of the patterns have the same arrangement of lines with approximately the same variation in intensity. As the calcium carbonate is replaced by manganese carbonate, however, the distance of a certain line from the

undeviated, or zero beam becomes greater until it reaches a maximum in rhodochrosite. The distances from the zero beam are measured in millimeters, and the interplanar spacings are computed according to the well-known formula of Bragg,<sup>14</sup>  $n\lambda = 2d \sin\theta$ . The interplanar spacings are given above each line in Figure 2, in Ångstrom Units ( $\times 10^{-8}$  cm.) and represent the distances between the atomic planes within the mineral. A few of the less intense lines, due to the decrease in reticular density with higher indices and consequent weakened reflecting power, could not be observed in all of the films. These have been put in as dotted lines and marked "unobserved" on the chart in approximately the position in which they should occur. These lines were observed in other films.

A decrease in the size of the unit rhombohedron,  $2d_{(100)}$  occurs throughout the series as the calcium atoms are replaced by the manganese atoms. The first line on the left of each  $x$ -ray diffraction pattern (Fig. 2) is produced by reflection from the atomic planes whose spacing varies from 3.075 Ångstrom units in calcite to 2.850 Ångstrom units in rhodochrosite. In the manganese mineral, therefore, these atomic planes are more closely spaced, and consequently some of the atomic diameters are smaller. Since the manganese and calcium atoms provide the only variables in the series it is to be inferred that the variation is due to the replacement of the calcium atoms by manganese atoms in the atomic structure.

The variation is not limited to the first planes, but occurs throughout the whole group of lines in each diffraction pattern. Table 3 shows all of the variations compared with  $x$ -ray diffraction measurements for calcium carbonate given by Harrington.<sup>15</sup>

The difference between calcite and rhodochrosite can be readily seen in Figure 3, which shows the actual photographs of the diffraction patterns, and where calcite has been placed next to rhodochrosite for comparison.

The structure of the group has not been considered, having been previously determined by the Braggs<sup>16</sup> from  $x$ -ray spectrometer measurements, and by Wyckoff<sup>17</sup> from Laue photographs.

<sup>14</sup> Bragg, W. H. and W. L., *X-rays and Crystal Structure*, G. Bell and Sons, London. p. 106, 1924.

<sup>15</sup> Harrington, E. A., *Amer. Jour. Sci.*, 5th Series, vol. 13, p. 477, 1927.

<sup>16</sup> *Op. cit.*

<sup>17</sup> Wyckoff, R. G. W., *Amer. Jour. Sci.*, 4th Series, vol. 50, p. 317, 1920.

TABLE III

| Harrington        |                   | Manganocalcite     |       |       |       |       | Rhodochrosite            |
|-------------------|-------------------|--------------------|-------|-------|-------|-------|--------------------------|
| CaCO <sub>3</sub> | CaCO <sub>3</sub> | %MnCO <sub>3</sub> |       |       |       |       | 95.72% MnCO <sub>3</sub> |
| A.U.              | A.U.              | 1.09               | 7.00  | 15.40 | 32.34 | 42.17 | A.U.                     |
| 3.03              | 3.075             | 3.055              | 3.020 | 3.005 | 2.975 | 2.948 | 2.850                    |
| 2.49              | 2.522             | 2.500              | 2.491 | 2.472 | 2.455 | 2.400 | 2.389                    |
| 2.28              | 2.300             | 2.297              | 2.268 | 2.257 | 2.250 | 2.235 | 2.180                    |
| 2.10              | 2.110             | 2.105              | 2.085 | 2.070 | 2.060 | 2.038 | 1.990                    |
| 1.920             | 1.935             | 1.925              | 1.903 | 1.883 | 1.866 | 1.850 | 1.809                    |
| 1.870             | 1.880             | 1.875              | 1.862 | 1.845 | 1.833 | 1.808 | 1.762                    |
| 1.602             | 1.613             | 1.608              | 1.599 | 1.589 | 1.575 | 1.561 | 1.540                    |
| 1.520             | 1.525             | 1.513              | 1.515 | 1.505 | 1.486 | 1.480 | 1.457                    |
| 1.437             | 1.450             | 1.438              | 1.435 | 1.425 | 1.413 | 1.402 | 1.378                    |
| 1.355             |                   |                    |       | 1.394 | 1.378 | 1.370 | 1.309                    |
|                   | 1.347             | 1.337              | 1.325 | 1.320 | 1.306 | 1.296 | 1.258                    |
| 1.295             | 1.306             | 1.300              | 1.285 | 1.275 | 1.267 | 1.253 | 1.222                    |
|                   |                   |                    | 1.248 | 1.239 | 1.233 | 1.217 | 1.197                    |
| 1.235             | 1.242             | 1.233              | 1.223 | 1.214 | 1.200 | 1.191 |                          |
| 1.178             | 1.190             | 1.181              | 1.168 | 1.158 | 1.144 | 1.140 | 1.128                    |
| 1.149             | 1.156             | 1.145              | 1.138 | 1.130 | 1.125 | 1.123 | 1.100                    |
| 1.044             | 1.045             | 1.042              | 1.037 | 1.028 | 1.023 | 1.010 | 0.985                    |
| 1.014             | 1.017             | 1.015              | 1.000 | 0.995 | 0.985 | 0.980 | 0.943                    |
| 0.984             | 0.988             | 0.985              | 0.973 | 0.969 | 0.961 | 0.960 |                          |
| 0.965             | 0.970             | 0.965              | 0.960 | 0.951 | 0.942 | 0.938 | 0.900                    |
| 0.943             | 0.945             | 0.940              | 0.934 | 0.929 | 0.920 | 0.918 | 0.880                    |
|                   | 0.895             | 0.890              | 0.885 | 0.880 | 0.875 | 0.869 | 0.850                    |
|                   | 0.854             | 0.850              | 0.844 | 0.839 | 0.835 | 0.929 | 0.812                    |
|                   | 0.836             | 0.833              |       | 0.819 | 0.810 | 0.805 |                          |
|                   | 0.799             | 0.797              | 0.790 |       |       | 0.780 | 0.760                    |
|                   | 0.790             | 0.786              | 0.780 | 0.774 | 0.768 | 0.761 |                          |





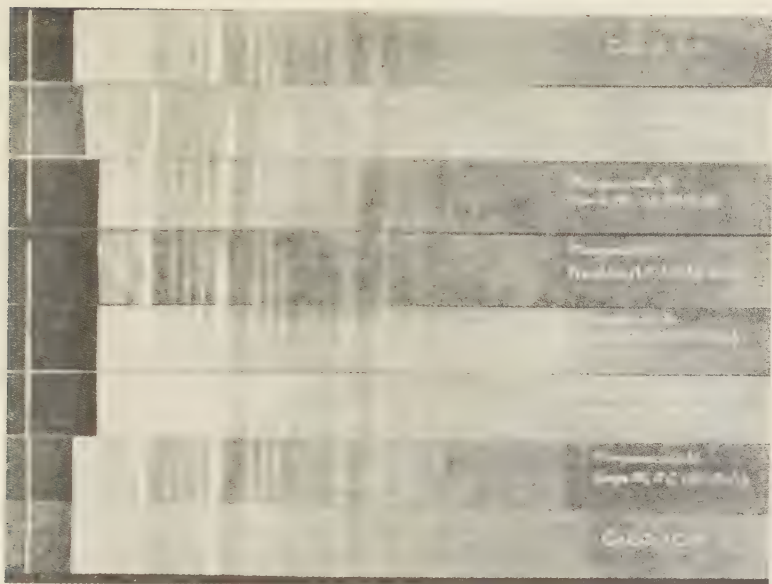


FIG. 3. Reproduction of  $x$ -ray diffraction patterns arranged in the order of increasing manganese carbonate content. A calcite pattern is placed above the one of rhodochrosite for comparison. See Figure 2 for interpretation of patterns.

### CONCLUSION

Data obtained by a study of the indices of refraction, specific gravities, and  $x$ -ray diffraction patterns of manganocalcite show a uniform variation within experimental limits depending upon the chemical composition. A study of five specimens of manganocalcite shows a definite relationship between the per cent of manganese carbonate and the physical or structural, and optical properties. The relation of the manganese carbonate content to the specific gravity is indicated by a gradual rise in value as the calcium carbonate is replaced by manganese carbonate until the composition of rhodochrosite is reached. The indices of refraction show an increase in both  $\epsilon$  and  $\omega$  as the per cent of manganese carbonate increases, approaching those of rhodochrosite as a limit. The first line of the diffraction patterns varies from 3.075 Ångstrom units in calcite to 2.850 Ångstrom units in rhodochrosite.

# ON THE OCCURRENCE OF BERYLLIUM IN THE ZINC DEPOSITS OF FRANKLIN, NEW JERSEY

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AND

L. H. BAUER, *New Jersey Zinc Company*.

In the spring of 1929, the junior author discovered the presence of beryllium in crystals of a complex silicate of unknown nature newly found at Franklin. Crystallographic and optical tests established the nature of this silicate as vesuvianite, a determination with which the analysis was in agreement. It was further found that cyprine from the same deposit showed the presence of beryllium spectroscopically although not in the same abundance.

In August another unrecognized mineral was found at Franklin which upon analysis proved to be the beryllium-barium silicate berylite, previously known only at Långban, Sweden. These minerals are described in the following pages.

The presence of beryllium in the Franklin ores is of uncommon interest. The present intensive search for adequate supplies of beryllium ores with which to establish the manufacture of this valuable metal makes any new occurrence of the element important. Unfortunately these beryllium minerals occur in veins of moderate extent. But if, as will be shown later to be probable, beryllium is really a normal constituent of vesuvianite then a new source of this element may be available. The probability that beryllium would be found at Franklin in some form was foretold by the observation of the German spectroscopist Eberhard<sup>1</sup> in 1912 of beryllium lines in the arc spectrum of willemite from that place. It appears however from these new discoveries that the beryllium is not typically associated with primary willemite ore but is a post-ore element introduced into the deposit by the contact action of the granite pegmatites as described by Palache.<sup>2</sup>

The vesuvianite occurs in the form of slender brown prisms embedded in a coarsely granular mixture of green willemite, brown garnet, leucophoenicite and barite with subordinate amounts of svabite, native copper and gageite. This is a typical paragenesis for veins of pegmatitic (high temperature) derivation.

The crystals show a simple combination of the common vesuvianite forms,  $p(111)$ ,  $m(110)$  and  $a(100)$ . They are of poor quality

<sup>1</sup> Liebis, *Sitzb. d. preuss. Akad. Wiss.*, **13**, 229, 1912.

<sup>2</sup> Palache, *Am. Mineral.*, **14**, 1, 1929.

for measurement as is so often the case with crystals of this substance. Thirteen values of  $\rho$  for (111) on four crystals gave an average angle of  $36^\circ 52'$  with the range  $36^\circ 26' - 37^\circ 13'$ . This corresponds to the element  $c = p_0 = 0.5303$ . Dana, *System*,  $c = 0.5372$ . It is optically uniaxial, negative, with absorption in brown,  $\omega > \epsilon$   $\omega = 1.712$ ;  $\epsilon = 1.700$ . Specific Gravity  $3.385 \pm .002$ .

The chemical analysis of a sample of picked crystals, by L. H. Bauer follows:

## ANALYSIS OF BE-VESUVIANITE

|                                       | 1.<br>Percentages | 2.<br>Mol. Ratios | 3.<br>Mol. Ratios |
|---------------------------------------|-------------------|-------------------|-------------------|
| SiO <sub>2</sub>                      | 34.25             | .568              | 6X .095           |
| CaO                                   | 33.15             | .591              | 6X .099           |
| BeO                                   | 9.20              | .367              | 4X .092           |
| MgO                                   | 3.17              | .079              |                   |
| MnO                                   | 4.84              | .068              | 2X .103           |
| ZnO                                   | 4.86              | .060              |                   |
| Al <sub>2</sub> O <sub>3</sub> (FeO*) | 9.70              | .095              | 1X .095           |
| H <sub>2</sub> O                      | 1.31              | .073              |                   |
|                                       | 100.48            |                   |                   |

\* FeO trace.

This analysis yields very exactly the formula  $2RO \cdot 6CaO \cdot 4BeO \cdot Al_2O_3 \cdot 6SiO_2$  where  $R = Mg, Mn$ , and  $Zn$  in about equal proportions. The small amount of  $H_2O$  is ignored as probably unessential. It will be noted in column 3 above that the ratios come out with great exactness. This is noteworthy particularly because in general the molecular ratios derived from vesuvianite analyses yield no such simple formula. It seems highly probable that beryllium is generally present in this mineral but has not been recognized, being determined as alumina. This, because of the very low molecular weight of  $BeO$ , would affect the ratios to a large degree. A chemical examination of other occurrences of vesuvianite for a possible beryllium content will therefore be of much interest and will be an early subject of investigation.

The form of vesuvianite known as cyprine is well known at Franklin and has been frequently analyzed. None of the analyses yield a simple ratio. It has now been established by Mr. Nitchie of the New Jersey Zinc Company's chemical staff at Palmerton, Pa., that cyprine shows spectroscopically strong lines of beryllium al-

though relatively less strong than in spectrograms of the brown Be-vesuvianite.

#### BARYLITE

Barylite was first described fifty years ago as an aluminum barium silicate occurring at Långban in association with hedyphane. It was not until 1923 that a new examination by Aminoff proved that the supposed alumina was really beryllium oxide. Barylite was first found at Franklin last August in specimens of hedyphane and calcite. It was first seen on the picking table but was later found in the mine in 960 pillar, 20 feet below the 400 foot level North about 15 feet from the hanging wall.

Attention was first drawn to the mineral by its vivid blue fluorescence in ultra-violet light, a color not previously yielded by any Franklin mineral. The following analysis by Mr. Bauer was made on selected fragments of the fluorescent substance:

|                                | BARYLITE    |             |
|--------------------------------|-------------|-------------|
|                                | 1.          | 2.          |
|                                | Percentages | Mol. Ratios |
| SiO <sub>2</sub>               | 36.42       | .604        |
| BaO                            | 46.49       | .302        |
| BeO                            | 15.77       | .628        |
| Al <sub>2</sub> O <sub>3</sub> | —           |             |
| MnO                            | —           |             |
| FeO                            | .19         |             |
| CaO                            | —           |             |
| MgO                            | .29         |             |
| ZnO                            | present     |             |
| PbO                            | .11         |             |
| H <sub>2</sub> O 110°C         | .40         |             |
|                                | 99.67       |             |

Examination of the analysis and derived molecular ratios shows that it is extremely pure material, yielding with great exactness the formula  $2\text{BeO} \cdot \text{BaO} \cdot 2\text{SiO}_2$ .

It may be observed that the BeO content of barylite, nearly 16 per cent, is higher by 2 per cent than that of beryl, the commonest beryllium compound.

The Franklin barylite is in plates embedded in hedyphane with some willemite. The single specimen seen is clearly part of a well banded vein, the succession of bands from a surface of ore being

(a) brown calcite and native copper; (b) gray calcite; (c) narrow zone of willemite and serpentine; (d) white calcite in curved rhombohedra, strongly fluorescent in ultra-violet light; (e) barylite, hedyphane and willemite. The barylite plates are more or less brecciated and are cemented with thin films of serpentine.

Barylite is white, 7 in hardness, and shows two good cleavages, one basal (001) and the other parallel to the pinacoid (100). Specific Gravity  $4.066 \pm .002$ . Optical properties (determined by H. Berman) are:

Biaxial, negative,  $2V = 70^\circ \pm 2^\circ$

(measured on Fedorow stage)

$$\alpha = 1.695 \pm .002$$

$$\beta = 1.702 \pm .002$$

$$\gamma = 1.708 \pm .002$$

Cleavages normal to  $\gamma$  and  $\beta$ .

These data differ somewhat from those given by Aminoff (re-measured by Berman) for the Långban mineral, which has somewhat lower indices of refraction, a slightly lower specific gravity, and the opposite optical sign in most cases. It is also to be noted that two cleavages are here reported whereas but one is given by Aminoff.

## DICKITE, A KAOLIN MINERAL

CLARENCE S. ROSS, *U. S. Geological Survey*,\*

AND

PAUL F. KERR, *Columbia University*.

The clay minerals have been under investigation in the laboratories of the U. S. Geological Survey, the U. S. National Museum, and Columbia University for several years. The study of the kaolin group of the clay minerals has been completed and a detailed report submitted for publication by the U. S. Geological Survey. This investigation has indicated the necessity of proposing one new mineral name for the kaolin mineral whose type locality is Almwch, Island of Anglesey, which it seems advisable to make immediately available to mineralogists. The study of the Anglesey mineral by Allan B. Dick, work so carefully done that the present paper adds no essential details, suggests the propriety of the name "dickite" for this kaolin mineral.

It has heretofore been commonly assumed that there was a single kaolin mineral, but the report mentioned will show that there are at least three distinct kaolin minerals—kaolinite, dickite, and nacrite. The question of nomenclature has proven a most vexing one. The literature is so extensive and the problem so involved that its discussion alone would exceed the length permissible in this paper. The conclusions, however, can be briefly outlined—conclusions concurred in by Doctors Edgar T. Wherry, W. T. Schaller, and W. F. Foshag.

Of the three kaolin minerals, one—the least abundant from near Freiberg, Saxony, has formerly been rather consistently called nacrite,<sup>1</sup> and so its nomenclature was rather simply solved by reviving this old name and giving it species rank.

In proposing the name kaolinite Johnson and Blake<sup>2</sup> clearly intended the name kaolinite to apply to the mineral characteristic of commercial kaolins, of which they studied many samples. The kaolinite of Johnson and Blake, however, included nacrite and probably the mineral from Anglesey, although the latter mineral would be excluded from their kaolinite by the optical data given by

\* Published by permission of the Director of the U. S. Geological Survey.

<sup>1</sup> Brongniart, A., *Traité élémentaire minérales*, vol. 1, p. 506, 1807.

Breithaupt, A., *Vollständige Charakteristik des Mineral-Systems*, 2d ed., p. 318, 1832,

<sup>2</sup> Johnson, S. W., and Blake, John M., On kaolinite and pholerite: *Am. Jour. Sci.*, 2d ser., vol. 43, pp. 351–361, 1867.

them. The Anglesey mineral, (dickite), which is also well known from Red Mountain, near Ouray, Colorado, seems always to have been included under kaolinite by subsequent writers. It exhibits the most perfect crystals of any known clay mineral and has been fully characterized by previous investigators.<sup>3</sup>

The assumption of a single kaolin mineral, and the existence of good optical data for only the Anglesey mineral has led many mineralogists to accept these data as correct for kaolinite. If the name kaolinite be applied to the Anglesey mineral—here called—dickite—the optical properties widely assigned to kaolinite would be retained, but this would mean that kaolinite rarely if ever occurred in kaolin and most of the references in the literature would be in error. On the other hand if the name kaolinite be retained for the dominant mineral of kaolin, the references for kaolinite will still apply for the most part but the optical properties will have to be revised. The name kaolinite has become so widely used and so firmly fixed in the literature that it seems imperative to retain it for the kaolin mineral that characterizes nearly all kaolin deposits. It then becomes necessary to give a new name to the Anglesey mineral.

The properties of dickite are shown in the following table which also gives the corresponding properties for the other two kaolin minerals—kaolinite and nacrite.

It will be seen from Table I that dickite can readily be distinguished from kaolinite by optical means where crystals are available. The acute bisectrix of kaolinite is nearly perpendicular to the perfect basal cleavage, while that of dickite is perpendicular to the edge of the crystal plates when they lie on the *b* faces. The optical character of kaolinite is (+), that of dickite (−). The dispersion of kaolinite is  $\rho < \nu$  and that of dickite  $\rho > \nu$ . The angle of extinction of kaolinite is small, usually difficult to determine, while that of dickite is  $15^\circ$  to  $20^\circ$ . There is a marked difference in the angle of extinction for blue and red in dickite while kaolinite and nacrite do not show this property.

Nacrite resembles dickite more closely than kaolinite, and except in very good crystals the two may be hard to distinguish by optical means.

<sup>3</sup> Dick, Allan B., On kaolinite: *Mineralog. Mag.*, vol. 8, pp. 15–27, 1888. Also, Supplementary note on the mineral kaolinite: *Mineralog. Mag.*, vol. 15, pp. 124–127, 1908.

Miers, H. A., *Mineralog. Mag.*, vol. 8, p. 25, 1888; vol. 9, p. 4, 1890.

TABLE I  
COMPARISON OF THE PROPERTIES OF THE KAOLIN MINERALS  
(Similarities)

|                                   | Nacrite                                                                                        | Dickite                                                               | Kaolinite                                                                                  |
|-----------------------------------|------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| Chemical composition              | $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$                          | $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ | $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2 \pm \text{SiO}_2$                 |
| Crystal system                    | Monoclinic                                                                                     | Monoclinic                                                            | Monoclinic                                                                                 |
| Orientation of the axial plane, A | $A \perp (010)$ , nearly $\parallel (100)$                                                     | $A \perp (010)$ , nearly $\parallel (100)$                            | $A \perp (010)$ , nearly $\parallel (100)$                                                 |
| Indices of refraction             | $\alpha = 1.557$<br>$\beta = 1.562$<br>$\gamma = 1.563$                                        | $\alpha = 1.560$<br>$\beta = 1.562$<br>$\gamma = 1.566$               | $\alpha = 1.561$<br>$\beta = 1.565$<br>$\gamma = 1.566$                                    |
| General appearance                | (Dissimilarities)                                                                              |                                                                       |                                                                                            |
|                                   | Nacrite                                                                                        | Dickite                                                               | Kaolinite                                                                                  |
|                                   | Pearly luster, fairly transparent<br>Trilled tabular crystals<br>Wedge-shaped cleavage plates. | Transparent, tabular crystals                                         | Translucent to opaque<br>Crystals elongated parallel to <i>c</i> axis<br>Vermicular habit. |

TABLE I (Continued).

|                                            | Nacrite                                                                    | Dickite                                                                    | Kaolinite                                                                           |
|--------------------------------------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Orientation of bisectrices                 | $Bx_a = X \wedge$ base normal = $10^\circ-12^\circ$<br>$Bx_o = Z = b$ axis | $Bx_o = X \wedge$ base normal = $15^\circ-20^\circ$<br>$Bx_a = Z = b$ axis | $Bx_a = X \wedge$ base normal = $1^\circ-3\frac{1}{2}^\circ$<br>$Bx_o = Z = b$ axis |
| Dispersion                                 | $\rho > \nu$ rarely $\rho < \nu$                                           | $\rho < \nu$                                                               | $\rho > \nu$                                                                        |
| Optical character                          | (-) rarely (+)                                                             | (+)                                                                        | (-)                                                                                 |
| Angle of extinction on (010) against base  | $1^\circ-3\frac{1}{2}^\circ$                                               | $15^\circ-20^\circ$                                                        | $10^\circ-12^\circ$                                                                 |
| Angle of extinction for red and blue light | Not different                                                              | Red $3^\circ$ greater than blue                                            | Not different                                                                       |
| X-ray diffraction pattern                  | Distinct for each species                                                  |                                                                            |                                                                                     |
| Dehydration curve                          |                                                                            |                                                                            |                                                                                     |
| Staining with dyes                         | Not readily stained by dyes<br>Not pleochroic                              | Not strongly stained by dyes<br>Not pleochroic                             | Adsorbs dyes very strongly, becoming pleochroic                                     |

TABLE II  
TABLE OF INTERPLANAR SPACING IN ÅNGSTROM UNITS  
FOR NACRITE, DICKITE, AND KAOLINITE

| Nacrite*         |                                            |              | Dickite*         |                                         |              | Kaolinite*       |                                         |              |
|------------------|--------------------------------------------|--------------|------------------|-----------------------------------------|--------------|------------------|-----------------------------------------|--------------|
| Arc<br>in<br>mm. | Spacing<br>in Å.U.<br>×10 <sup>-8</sup> cm | Est.<br>Int. | Arc<br>in<br>mm. | Spacing<br>in Å.U.<br>×10 <sup>-8</sup> | Est.<br>Int. | Arc<br>in<br>mm. | Spacing<br>in Å.U.<br>×10 <sup>-8</sup> | Est.<br>Int. |
| 18.3             | 4.471                                      | 8            | 18.3             | 4.471                                   | 8            | 18.3             | 4.464                                   | 10           |
| 19.5             | 4.201                                      | 5            | 19.5             | 4.201                                   | 5            | 19.5             | 4.194                                   | 10           |
| 22.6             | 3.621                                      | 9            | 21.3             | 3.846                                   | 5            | 21.1             | 3.874                                   | 5            |
| 24.25            | 3.371                                      | 4            | 22.55            | 3.631                                   | 9            | 22.6             | 3.614                                   | 6            |
| 26.4             | 3.101                                      | 3            | 23.5             | 3.491                                   | 2            | 23.9             | 3.424                                   | 5            |
| 32.2             | 2.541                                      | 5            | 24.6             | 3.336                                   | .5           | 25.8             | 3.069                                   | 2            |
| 33.8             | 2.425                                      | 10           | 25.9             | 3.161                                   | .5           | 29.3             | 2.789                                   | 1            |
| 35.1             | 2.335                                      | 4            | 27.5             | 2.981                                   | 2            | 32.6             | 2.512                                   | 9            |
| 39.1             | 2.095                                      | 4            | 28.8             | 2.741                                   | 2            | 34.8             | 2.344                                   | 10           |
| 41.4             | 1.980                                      | 5            | 31.6             | 2.591                                   | 5            | 35.6             | 2.305                                   | 4            |
| 42.7             | 1.920                                      | 5            | 32.4             | 2.526                                   | 8            | 37.2             | 2.205                                   | 1            |
| 45.1             | 1.820                                      | 2            | 34.0             | 2.408                                   | 1            | 41.0             | 2.005                                   | 4            |
| 49.3             | 1.671                                      | 5            | 35.0             | 2.346                                   | 10           | 44.3             | 1.860                                   | 1            |
| 55.5             | 1.480                                      | 9            | 36.9             | 2.225                                   | 2            | 49.4             | 1.666                                   | 6            |
| 56.6             | 1.450                                      | 3            | 41.2             | 1.995                                   | 8            | 50.6             | 1.621                                   | 2            |
| 60.0             | 1.368                                      | 4            | 42.9             | 1.910                                   | 1            | 53.1             | 1.549                                   | 2            |
| 62.5             | 1.318                                      | 1            | 43.9             | 1.870                                   | 2            | 55.3             | 1.487                                   | 6            |
| 65.4             | 1.273                                      | 4            | 45.6             | 1.800                                   | 1            | 56.6             | 1.455                                   | 2            |
| 67.2             | 1.230                                      | 2            | 49.7             | 1.659                                   | 9            | 59.4             | 1.382                                   | 1            |
| 68.5             | 1.209                                      | 5            | 52.7             | 1.564                                   | 5            | 61.6             | 1.347                                   | 5            |
| 70.1             | 1.179                                      | 1            | 55.2             | 1.494                                   | 8            | 63.4             | 1.303                                   | 2            |
| 72.9             | 1.134                                      | .25          | 56.2             | 1.469                                   | 2            | 64.4             | 1.283                                   | 3            |
| 75.8             | 1.094                                      | .25          | 57.4             | 1.434                                   | .5           | 66.9             | 1.233                                   | 4            |
| 76.8             | 1.079                                      | .25          | 58.6             | 1.409                                   | 1            | 68.8             | 1.203                                   | .5           |
| 80.8             | 1.028                                      | .5           | 59.7             | 1.383                                   | 1            | 71.3             | 1.164                                   | .25          |
| 87.0             | .959                                       | .5           | 62.4             | 1.323                                   | 8            | 74.5             | 1.114                                   | .25          |
| 91.9             | .910                                       | .25          | 63.9             | 1.293                                   | 3            | 76.5             | 1.084                                   | .25          |
| 98.1             | .854                                       | .25          | 65.7             | 1.258                                   | 4            | 79.8             | 1.041                                   | .25          |
| 101.2            | .833                                       | .25          | 66.9             | 1.236                                   | 4            | 82.1             | 1.013                                   | .25          |
| 106.0            | .798                                       | .25          | 69.4             | 1.190                                   | 3            | 87.9             | .951                                    | .5           |
| 115.7            | .737                                       | .25          | 71.6             | 1.159                                   | .5           | 94.3             | .889                                    | .5           |
| 121.0            | .707                                       | .25          | 75.0             | 1.109                                   | 2            | 98.0             | .858                                    | .25          |
|                  |                                            |              | 77.1             | 1.077                                   | 1            | 100.7            | .838                                    | .25          |
|                  |                                            |              | 80.3             | 1.032                                   | 2            | 106.1            | .797                                    | .25          |
|                  |                                            |              | 83.9             | .995                                    | 1            |                  |                                         |              |
|                  |                                            |              | 87.0             | .960                                    | 1            |                  |                                         |              |
|                  |                                            |              | 89.8             | .930                                    | 1            |                  |                                         |              |
|                  |                                            |              | 94.4             | .879                                    | 2            |                  |                                         |              |
|                  |                                            |              | 97.6             | .859                                    | .25          |                  |                                         |              |
|                  |                                            |              | 99.9             | .842                                    | .25          |                  |                                         |              |
|                  |                                            |              | 102.5            | .820                                    | .5           |                  |                                         |              |
|                  |                                            |              | 110.6            | .765                                    | .25          |                  |                                         |              |
|                  |                                            |              | 115.6            | .735                                    | .25          |                  |                                         |              |

\* Corrected against sodium chloride (100)=2.814 Å.U. (measurements in millimeters are given as read on film. Å.U. measurements include a small correction based on sodium chloride).

Table 2 (the interplanar spacings) shows that all three minerals have very distinct *x*-ray properties.<sup>4</sup>

The chemical composition of dickite is that commonly accepted for kaolinite, namely,  $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . Kaolinite shows a variation from this formula which will be discussed in the forthcoming paper.

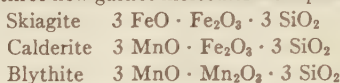
<sup>4</sup> Interplanar spacings in Table 2 are computed from direct measurement of photographs by the formula  $n\lambda = 2d \sin \theta$ ; where  $\theta = 90(\text{arc in mm.}/\pi r)$ ,  $r = 114.59 \text{ mm.}$  and  $\lambda = .71212 \text{ \AA.U.}$

## NOTES AND NEWS

### SPESSARTITE FROM AVONDALE, DELAWARE COUNTY, PENNSYLVANIA

LESTER W. STROCK, *Academy of Natural Sciences of Philadelphia.*

In 1926 L. Leigh Fermor,<sup>1</sup> after a study of several garnets from India, arrived at the conclusion that three new garnet molecules were present, which he called:



Subsequently, Shannon analyzed a garnet from Amelia, Virginia,<sup>2</sup> and from Gwynns Falls, Baltimore, Md.<sup>3</sup> Both of these garnets contain considerable manganese. By calculating a portion of the manganese found as the new molecule "blythite," Shannon was able to derive a formula for the Amelia garnet which gave better agreement with the garnet formula.

The large garnet crystals from Avondale, so conspicuous in every large collection, are likewise sufficiently high in manganese to be classified as the spessartite variety. It was thought advisable to reinvestigate the Avondale garnet,<sup>4</sup> employing all the necessary precautions which are so indispensable in mineral analysis, and exercising special care in the accurate separation of iron, manganese and aluminum.

**LOCALITY.** The garnet crystals are found in Leiper's Quarry, Avondale, on the east bank of Crum Creek one mile south of Swarthmore, Delaware County, Pennsylvania.<sup>5</sup>

**GEOLOGY.** The quarry is situated on the coastal plain of the Philadelphia District, in a granite gneiss that according to F. Bascom<sup>6</sup> is of early Cambrian age or older. Crum Creek has cut down through the thin cap of the overlying coastal plain of sedimentary formation, the Pensauken, and exposed the granite gneiss along this portion of its course. Cutting the granite gneiss are veins of pegmatite, in which the garnets occur, associated with black tourmaline, beryl, apatite, feldspar, muscovite, and occasionally secondary torbernite.

**DESCRIPTION OF SPECIMEN.** A specimen from the collection of the Academy of Natural Sciences of Philadelphia was selected for study. The crystal was roughly two inches in diameter, of slightly distorted trapezohedral form, modified by very small dodecahedral faces. One-third of the crystal was in contact with pegmatite matrix, consisting of muscovite, quartz, and microcline. Broken parts of two other smaller crystals were attached to the larger crystal. The trapezohedron was the (211) form, as determined by measurement of the interfacial angles (48 and 33 degrees) using a Penfield contact goniometer.

A broken corner from the larger crystal was removed for analysis and for physical determinations. The mineral was crushed to fragments of 1 mm. size in an agate mortar and examined with the microscope. All fragments attached to or containing any impurity were discarded; the main impurities being quartz, feldspar, and mica. These minerals occurred scattered through the garnet in considerable quantity even though the crystal appeared very clear. All the clear glassy grains were separated and crushed finer, and all impurities again sorted out. Only perfectly clear grains were used for the analysis. The powder when examined under polarized light was found to be homogeneous and isotropic. The powdered mineral was pale salmon in color.

## PHYSICAL DETERMINATIONS

**REFRACTIVE INDEX.** The index of refraction was determined by the powder immersion method, and the index of the liquid ascertained on a goniometer by means of a hollow  $30^\circ$  prism. This gave the value  $n=1.805$ .

**SPECIFIC GRAVITY.** The specific gravity was determined by adjusting a Clerici solution until grains neither floated nor sank. The gravity of the solution was then determined by means of a pycnometer. The value 4.117 was obtained.

## CHEMICAL ANALYSIS

The analytical methods recommended by H. S. Washington<sup>7</sup> for the determination and separation of the various elements occurring in minerals, were closely followed. The sample used weighed 0.5895 grams. The details of the various operations will be omitted, but the greatest care was exercised as to technique, cleanliness, purity of reagents, and proper removal of excess salts before attempting to precipitate any element.

It is necessary to emphasize the point that considerable  $\text{SiO}_2$  comes down with the iron and aluminum and even with calcium, and that some iron and aluminum also precipitate with  $\text{SiO}_2$ . Therefore it is necessary to separate these precipitates and return the second or contaminating elements to their proper portions. Titanium was tested for but found absent.

## ANALYSIS OF SPESSARTITE

Leiper's Quarry, Avondale, Delaware Co., Pa.

Lester W. Strock, Analyst.

|                         | I        | II             | III                     | IV                    | V                             | VI           |
|-------------------------|----------|----------------|-------------------------|-----------------------|-------------------------------|--------------|
|                         | Analysis | Mol.<br>Ratios | Spessartite<br>Molecule | Almandite<br>Molecule | Grossu-<br>larite<br>Molecule | Sum<br>III-V |
| $\text{SiO}_2$          | 36.52    | 0.6084         | 0.3722                  | 0.1983                | 0.0336                        | 0.6042       |
| $\text{Al}_2\text{O}_3$ | 21.00    | 0.2055         | 0.1241                  | 0.0661                | 0.0112                        | 0.2014       |
| FeO                     | 14.27    | 0.1983         |                         | 0.1983                |                               | 0.1983       |
| MnO                     | 26.41    | 0.3723         | 0.3723                  |                       |                               | 0.3723       |
| CaO                     | 1.88     | 0.0336         |                         |                       | .0336                         | 0.0336       |
|                         | 100.08   |                |                         |                       |                               |              |
| Mol. percentages        |          |                | 61.6                    | 32.8                  | 5.6                           |              |

It will be seen from the above that the Avondale garnet is a member of the almandite—spessartite series, with spessartite as the major constituent. Most of the garnets of granite pegmatite belong to this series.<sup>3</sup> Ford<sup>8</sup> has pointed out that whenever a garnet contains three constituent molecules, two are always present in larger amounts, while the third is present as a minor constituent—less than 10 per cent of the whole. This is true of the Avondale garnet.

It was not necessary to assume any manganese present in the trivalent state, as a "blythite" molecule, in order to compute a satisfactory formula; the analysis shows a slight excess of  $\text{R}_2\text{O}_3$ , which however is within the limit of analytical error.

## REFERENCES

- <sup>1</sup> L. Leigh Fermor, On the composition of some Indian garnets. *Records Geol. Surv. India*, Vol. 59, Pt. 2, 191-207, 1926. This reference by Shannon is erroneously given as Vol. 49 instead of Vol. 59.
- <sup>2</sup> Earl V. Shannon, "Blythite" and the manganese garnet from Amelia, Virginia. *Jour. Wash. Acad. Science*, Vol. 17, No. 17, Oct. 19, 1927.
- <sup>3</sup> Shannon and Gonyer, Almandite and spessartite garnet from Gwynns Falls, Baltimore, Md. *Jour. Wash. Acad. Science*, Vol. 17, No. 21, Dec. 19, 1927.
- <sup>4</sup> W. C. Robinson, Analysis of Spessartite Garnets. (An analysis was made by Robinson under the direction of Genth in 1887.) *Jour. Analyt. Chem.*, 1, 251, 1887.
- <sup>5</sup> Mineralogy of Pennsylvania, Samuel G. Gordon, 1922, page 197.
- <sup>6</sup> F. Bascom, Pre-Triassic metamorphic rocks (Granite Gneiss). *Philadelphia Folio, U. S. Geol. Surv.*, No. 162, page 5, col. 4.
- <sup>7</sup> H. S. Washington, *Analysis of Rocks*, 3rd ed., New York, (1919).
- <sup>8</sup> W. E. Ford, A study of the relations existing between the chemical, optical and other physical properties of the members of the garnet group. *Amer. Jour. Science*, Vol. XL, page 33, 1915.

## BOOK REVIEWS

PRECIOUS AND SEMI-PRECIOUS STONES. MICHAEL WEINSTEIN. VIII +138 pp., with a colored frontispiece and 16 full page illustrations. Sir Isaac Pitman & Sons, Ltd., London, 1929.

This book aims to present the more important facts concerning gems in a concise, readable, and non-technical manner and should appeal to the general reader interested in precious and semi-precious stones.

The physical properties of gems, cutting of stones, artificial staining, and weight and prices are all considered briefly, as is also the subject of real, synthetic, and imitation stones. In the more general part most of the minerals used as gems, as well as pearl, amber, coral, and jet, are discussed. There is also a chapter entitled "Superstition and Gem Stones" and an appendix in which gem materials are arranged according to color, chemical composition, hardness, specific gravity, dichroism, indices of refraction, and locality.

While the material is on the whole well presented, there are a number of unpardonable errors. For example, the statements on pages 5 and 40 that nearly all synthetic stones are made in Germany and France and that "The term 'corundum' must not be confused with the abrasive material carborundum, which is corundum mixed with heavy minerals, such as magnetite and hematite, all of lower hardness," are incorrect and should be revised.

The frontispiece and the various half-tone illustrations are very good.

EDWARD H. KRAUS

DIAMOND—A DESCRIPTIVE TREATISE. J. R. SUTTON. XII+118, with 111 full page illustrations. Thomas Murby & Co., London, 1928.

This book is based largely upon observations over a period of 35 years in the diamond fields of Africa, and is designed for the general reader and lover of gem stones. Although the author gives much general information concerning the various

properties of the diamond, as well as its occurrence and origin, the chief value of the book lies in the emphasis placed upon the characteristics of the stones from different localities. The many full page illustrations add materially to the attractiveness of the text, for the half-tone cuts are especially good.

EDWARD H. KRAUS

ORE DEPOSITS OF MAGMATIC ORIGIN. PAUL NIGGLI. Translated from the original German edition by H. C. Boydell. XI+93 pages, 11 figures. Thomas Murby & Co., London. D. Van Nostrand Co., New York, 1929. Price \$3.50.

This book is an adaptation of a series of lectures presented at the Swiss Federal Technical University of Zürich in 1923-24 and published as Volume I of Niggli's "Abhandlungen zur praktische Geologie und Bergwirtschaftslehre." The translation by Dr. Boydell has been revised and supplemented by Dr. Niggli and Dr. R. L. Parker.

In this altogether too brief treatise, Dr. Niggli attempts to develop a logical and consistent classification of ore deposits of magmatic origin. Such a classification he believes must hold good not only for ore deposits but also for igneous rocks and *visa versa*, since as he says: "Ore deposition is a part problem of magmatic differentiation in its widest sense."

He points out that a systematic classification of igneous rocks may be founded on any one of the three following bases: (1) Physical and geological conditions prevailing at the place of formation, (2) Chemical and (or) mineralogical composition and (3) Provincial relationships; and then he discusses each in turn in its application to ore deposits. The result is one classification combining (1) and (2) and a second classification combining (1) and (3).

The discussion as presented in the book is already so condensed that further condensation in the form of an abstract is impossible.

CHAS. W. COOK

## PROCEEDINGS OF SOCIETIES

### NEW YORK MINERALOGICAL CLUB

#### *Minutes of the October Meeting*

A regular monthly meeting of the New York Mineralogical Club, attended by 39 members, was held at the American Museum of Natural History on the evening of October 16, 1929, with President Herbert P. Whitlock in the chair.

Mr. James Collins and Miss Ellen M. Shattuck of New York City, Mr. Ralph Pastor of Brooklyn, N. Y., and Mr. M. H. Clark of Newark, N. J., were elected to membership.

Mr. Manchester reported a successful Club trip to the quarries at Bedford, N. Y., on Decoration Day, May 30th, which was attended by about 30 persons.

The program of the evening consisted of short accounts of their summer experiences by various members, with exhibits of specimens. Among the latter were spear-shaped casts of prehnite after an undetermined mineral, from Paterson, N. J.; also calcite from the same locality; garnet from Bedford, N. Y.; iridescent pyrite from South River, N. J.; and a rose coated with calcium carbonate from the springs of Carlsbad, Germany.

Perhaps the most striking specimen was an unusually large and fine black tourmaline from Bedford, N. Y. As finally restored after being shattered in the quarry, the specimen consists of a radiating group of 32 crystals, 24 of which are terminated, and weighs about 22 kilos. The largest crystal is about 45 cms. long and 7 cms. in diameter.

HORACE R. BLANK, *Secretary*

#### PHILADELPHIA MINERALOGICAL SOCIETY

*Academy of Natural Sciences, Philadelphia*

*November, 7, 1929.*

A stated meeting of the Philadelphia Mineralogical Society was held on the above date, Mr. Toothaker presiding. Forty-three members and seven visitors were in attendance. Upon favorable recommendation of the Council the following were elected as senior members: Mr. Benjamin H. Shoemaker and Mr. Alexander Fleming. Mr. Cienkowski proposed Messrs. Albert Ackoff, James R. Eichna and Henry Guent for junior membership. The resignation of Mr. Horace R. Blank was accepted with regrets.

Mr. Harold W. Arndt addressed the Society on "*Recent Collecting in New England*." The speaker reported on the following localities: Kane and New Milford, Connecticut; Chester, Huntington, Cummington, Russell and Westfield, Massachusetts. At Kane, he reported the opening of a new quarry in the tremolite locality where he obtained some of the rare light variety of diopside and malaconite. He found the old quarries at New Milford, which produced much beryl in the past, no longer operating. Excellent margarite and diaspore were shown from Chester and spodumene crystals from Huntington. An exceptionally attractive specimen of pyrolusite was obtained by Mr. Arndt from a recently opened vein of managense at Cummington, and from an old collection he secured some of the famous melanite variety of andradite garnets originally found at Russell by a well-digger. At Westfield he found that much datolite was still obtainable and of good quality.

Mr. Toothaker gave an interesting account of a recent trip to Hot Springs, Magnet Cove and Crystal Springs, Arkansas. The Joplin District in Missouri, Oklahoma and Kansas were also visited and he was able to show some very fine examples of the specimens obtained from the various localities.

Mr. Cinkowski reported in a trip to the French Creek Mines, now closed, and indicated that specimens could still be obtained from the old dumps. Mr. Thacher was equally lucky on the old dumps at the Wheatley mines, near Phoenixville. Mr. Biernbaum presented the Society with a picture showing a pink tourmaline from Paris, Maine, which establishes a new record for size.

LESTER W. STROCK, *Secretary*